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CATALYTIC INTER-ESTERIFICATION

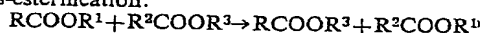
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No Drawing. Filed Aug. 8, 1963, Ser. No. 300,938
9 Claims. (Cl. 260—410.9)

The present invention relates to esterification techniques and, more particularly, to improved esterification procedures involving the use of unique catalytic materials.

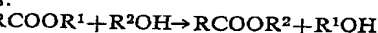
Ester interchange reactions are well known in the art and, generally speaking, comprise the reaction of an ester with another compound to form an ester different from the reactant ester. Such reactions have been referred to by various names including, though not restricted to, trans-esterification, ester exchange, re-esterification, etc.

Basically, there are three types of reactions falling within the above-mentioned category, the first being a straight trans-esterification involving the interaction of two different esters, the second involving the reaction between an ester and an alcohol (alcoholysis) and the third being the reaction between an ester and an acid (acidolysis). These reactions, all of which are equilibrium reactions, may be illustrated in equation form as follows:

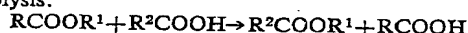
Trans-esterification:



Alcoholysis:



Acidolysis:



In the past, ester interchange reactions as set forth above have had many practical uses and, in fact, have provided an important approach to the synthesis of a variety of useful products. For example, such reactions have been used for the molecular re-arrangement of glycerol esters with mixtures of fatty acids, for effecting ester-ester interchange between aromatic carboxylic acid esters of monohydric alcohols (e.g., dimethyl phthalate) and low or high molecular weight aliphatic carboxylic acid esters of polyhydric alcohols such as glycerol (triacetin, trilinolein), etc. One significant limitation on the versatility of such ester exchange techniques has been, however, the nature of the particular catalyst utilized in the reaction. For example, many of the prior art catalysts have been acids or bases which have been unsatisfactory with certain compounds with which they react. Other compounds, less reactive, have often presented difficult separation problems. Still other catalysts have been short lived and, due to their nature, have not been readily regenerated.

In accordance with the present invention, it has now been discovered that ester exchange reactions as set forth above may be carried out extremely satisfactorily and economically by means of a unique class of catalytic materials, namely solid porous crystalline aluminosilicate zeolites. Such catalysts are not only effective for carrying out the ester exchange reactions set forth with high reaction rates and excellent yield but increase the commercial feasibility of the reaction since such crystalline aluminosilicates have extremely long life and may be readily regenerated for re-use.

It is accordingly a primary object of the present invention to provide a novel technique for conducting ester exchange reactions.

It is a further object of the present invention to provide a novel technique of carrying out an ester exchange reaction by means of solid porous crystalline aluminosilicate catalysts.

It is still another important object of the present invention to provide a novel method of carrying out ester exchange techniques under particularly practicable reaction

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conditions through the utilization of solid porous crystalline aluminosilicate zeolite catalysts.

It is a further important object of the present invention to catalytically promote the ester exchange reaction between a plurality of esters, between an ester and an alcohol and between an ester and an acid by means of crystalline aluminosilicate zeolite catalysts.

These and further important advantages and objects of the present invention will become more apparent upon reference to the ensuing description and appended claims.

Zeolitic materials, both natural and synthetic, in naturally occurring and modified forms, have been demonstrated in the past to have catalytic capabilities for various types of hydrocarbon conversion and other reactions involving the synthesis or modification of various organic materials. Such zeolitic materials are ordered crystalline aluminosilicates having a definite crystalline structure within which there are passages, pores or cavities of definite ranges of size. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials have come to be known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties.

The present invention, as aforesaid, involves the use of such zeolitic materials for the purpose of carrying out ester exchange reactions to form modified ester compounds under conditions which are extremely satisfactory for practical commercial operations and with surprisingly superior results.

The ester exchange reactions which may be carried out in accordance with the present invention are any of those reactions equations for which have previously been set forth. In these equations, all of the "R" substituents, viz., R through R³, may vary quite widely as is well known to those skilled in the art of ester exchange. Merely by way of example, the "R" substituents may be aliphatic, cycloaliphatic, aromatic, alicyclic, etc.

Illustrative of alcohols which may be used are the monohydric alcohols, including low molecular weight alcohols such as methyl, ethyl, propyl, butyl, allyl and benzyl alcohols, dimethyl carbinol, methyl ethyl carbinol, diethyl carbinol, methyl hexyl carbinol, diallyl carbinol, menthol, trimethyl carbinol, dimethyl propyl carbinol, phenol and thymol.

High molecular weight alcohols, such as those obtained from the hydrolysis of lanolin to produce lanolin alcohols, may also be used. The sterols, which include cholesterol, ischolesterol and the like, may be combined with certain acids to produce esters which have particular utility in the cosmetic industry.

In addition to the above, polyhydric alcohols may also be used in the practice of the present invention. Exemplary of such alcohols are ethylene glycol; 1,3-propylene glycol; 1,2-butylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,12-octadecylene glycol; diethylene glycol; triethylene glycol; hexylene glycol; glycerine; pentaerythritol; poly-3-chloro-1,2-propylene glycol; cyclopentylene glycol; sorbitol; triethanolamine; quercitol; etc.

The alcohols usable in the practice of the present invention may be saturated or unsaturated, with such unsaturation being olefinic or aromatic (or even acetylenic), and the alcohols may be either primary, secondary or tertiary. For example, all of the butyl alcohols, including n-butyl, isobutyl, secondary butyl and tertiary butyl alcohols, may be used.

The acids usable in the acidolysis reaction of the present invention include both monocarboxylic and polycarboxylic acids, both aliphatic and aromatic. Examples of usable acids are acetic; benzoic; butyric; heptanoic; formic; isobutyric; isovaleric; naphthoic; propionic; salicylic; valeric; acrylic; crotonic; hydrosorbic; undecylenic;

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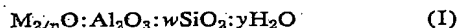
propionic; lauroleic; hydrocinnamic; benzoylacetic; furoic; abietic; caproic; caprylic; capric; lauric; pivalic; myristic; palmitic; p-phenyl benzoic; beta-naphthoic; stearic; oleic; linoleic; linolenic; fumaric; maleic; malic; malonic; oxalic; phthalic; terephthalic; pyrotartaric; succinic; tartaric; glutaric; adipic; pimelic; suberic; azaleic; sebacic; apocamphoric; diphenic; naphthalene-1,2-dicarboxylic; furfuralmalonic; dilinoleic; citric; tricarballic; aconitic; trilinoleic; hemimellitic; lactic; mandelic; ricinoleic; glycolic; hydracrylic; glyceric; quinic; caffeic; tropic; meconic; arachidic; behenic; lignoceric; myristoleic; palmitoleic; etc.

The esters utilizable in the practice of the present invention may be any ester, be it aliphatic or aromatic, of a carboxylic acid, such as esters of any of the carboxylic acids previously mentioned.

The aluminosilicates useable as catalysts in accordance with the present invention include a wide variety of positive ion-containing crystalline aluminosilicates, both natural and synthetic. These aluminosilicates can be described as a rigid three-dimensional network of SiO_4 and AlO_4 tetrahedra in which the tetrahedra are cross-linked by the sharing of oxygen atoms whereby the ratio of the total aluminum and silicon atoms to oxygen atoms is 1:2. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This equilibrium can be expressed by formula wherein the ratio of Al_2 to the number of the various cations, such as Ca, Sr, Na_2 , K_2 or Li_2 , is equal to unity. One cation may be exchanged either in entirety or partially by another cation utilizing ion exchange techniques as discussed hereinbelow. By means of such cation exchange, it is sometimes possible, or even desirable, to vary the size of the pores in the given aluminosilicate by suitable selection of the particular cation. The spaces between the tetrahedra are occupied by molecules of water prior to dehydration.

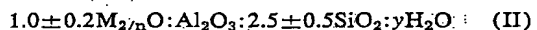
A description of zeolites of the type useable in the present invention is found in Patent 2,971,824, whose disclosure is hereby incorporated herein by reference. These aluminosilicates have well-defined intra-crystalline dimensions such that only reactant or product molecules of suitable size and shape may be transported in either direction between the exterior phase and the interior of the crystalline zeolite.

In their hydrated form, the aluminosilicates may be represented by the formula:



wherein M is a cation which balances the electrovalence of the tetrahedra, n represents the valence of the cation, w the moles of SiO_2 , and y the moles of H_2O , the removal of which produces the characteristic open network system. The cation may be any one or more of a number of positive ions as aforesaid, such ions being discussed in greater detail hereinafter. The parent zeolite is dehydrated to actuate it for use as a catalyst. Although the proportions of inorganic oxides in the silicates and their spatial arrangement may vary, effecting distinct properties in the aluminosilicates, the main characteristic of these materials is their ability to undergo dehydration without substantially affecting the SiO_4 and AlO_4 framework. In this respect, this characteristic is essential for obtaining catalyst compositions of high activity in accordance with the invention.

Representative materials include a synthetic faujasite, designated zeolite X, which can be represented in terms of mole ratios of oxides as follows:

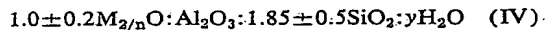


wherein M is a metal cation having a valence of not more than three, n represents the valence of M, and y is a value up to eight depending on the identity of M and degree of hydration of the crystal. The sodium form may

be represented in terms of mole ratios of oxides as follows:



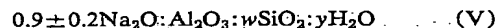
Another synthesized crystalline aluminosilicate, designated zeolite A, can be represented in mole ratios of oxides as:



wherein M represents a metal cation, n is the valence of M, and y is any value up to about 6. As usually prepared, zeolite A contains primarily sodium cations and is designated sodium zeolite A.

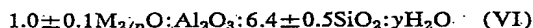
Other suitable synthesized crystalline aluminosilicates are those designated zeolite Y, L and D.

The formula for zeolite Y (which is a synthetic faujasite) expressed in oxide mole ratios is:



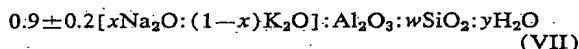
wherein w is a value ranging from 3 to 6 and y may be any value up to about 9.

The composition of zeolite L in oxide mole ratios may be represented as:



wherein M designates a metal cation, n represents the valence of M, and y is any value from 0 to 7.

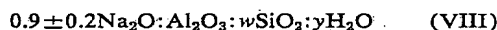
The formula for zeolite D, in terms of oxide mole ratios, may be represented as:



wherein x is a value of 0 to 1, w is from 4.5 to about 4.9 and y in the fully hydrated form, is about 7.

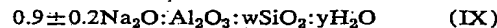
Other synthetic crystalline aluminosilicates which can be used include those designated as zeolite R, S, T, Z, E, F, Q and B.

The formula for zeolite R in terms of oxide mole ratios may be written as follows:



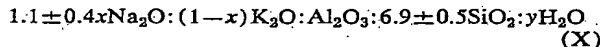
wherein w is from 2.45 to 3.65, and y , in the hydrated form, is about 7.

The formula for zeolite S in terms of oxide mole ratios may be written as:



wherein w is from 4.6 to 5.9 and y , in the hydrated form, is about 6 to 7.

The formula for zeolite T in terms of oxide mole ratios may be written as:



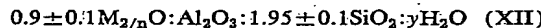
wherein x is any value from about 0.1 to about 0.8 and y is any value from about 0 to about 8.

The formula for zeolite Z in terms of oxide mole ratios may be written as:



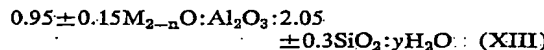
wherein y is any value not exceeding 3.

The formula for zeolite E in terms of oxide mole ratios may be written as:



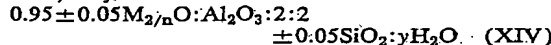
wherein M is a metal cation, n is the valence of the cation, and y is a value of 0 to 4.

The formula for zeolite F in terms of oxide mole ratios may be written as:



wherein M is a metal cation, n is the valence of the cation, y is any value from 0 to about 3.

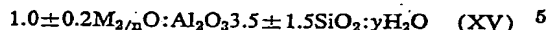
The formula for zeolite Q, expressed in terms of oxide mole ratios, may be written as:



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wherein M is a metal cation, n is the valence of the cation, and y is any value from 0 to 5.

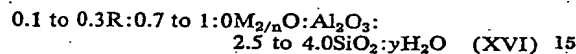
The formula for zeolite B may be written in terms of oxide mole ratios as:



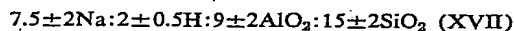
wherein M represents a metal cation, n is the valence of the cation, and y has an average value of 5.1 but may range from 0 to 6.

Other synthesized crystalline aluminosilicates include those designated as ZK-4 and ZK-5.

ZK-4 can be represented in terms of mole ratios of oxides as:



wherein R is a member selected from the group consisting of methylammonium oxide, hydrogen oxide and mixtures thereof with one another, M is a metal cation, n is the valence of the cation, and y is any value from about 3.5 to about 5.5. As usually synthesized, zeolite ZK-4 contains primarily sodium cations and can be represented by unit cell formula:

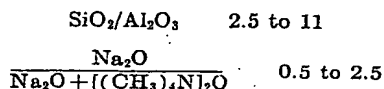


The major lines of the X-ray diffraction pattern of ZK-4 are set forth in Table 1 below:

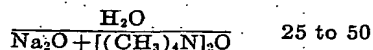
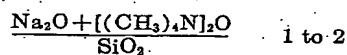
TABLE 1

d Value of reflection in Å.	100 I/I ₀
12.00	100
9.12	29
8.578	73
7.035	52
6.358	15
5.426	23
4.262	11
4.062	49
3.662	65
3.391	30
3.254	41
2.950	54
2.725	10
2.663	7
2.593	15
2.481	2
2.435	1
2.341	2
2.225	2
2.159	4
2.121	5
2.085	2
2.061	2
2.033	5
1.90	2
1.880	2
1.828	1
1.813	1
1.759	1
1.735	1
1.720	5
1.703	1
1.669	2
1.610	1
1.581	2
1.559	1

ZK-4 can be prepared by preparing an aqueous solution of oxides containing Na_2O , Al_2O_3 , SiO_2 , H_2O and tetramethyl-ammonium ion having a composition, in terms of oxide mole ratios, which falls within the following ranges:

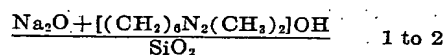
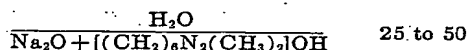
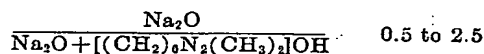


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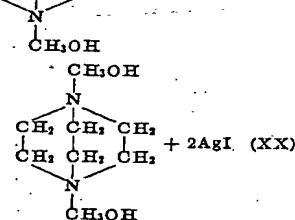
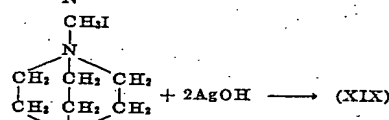
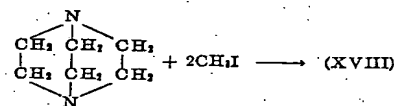


maintaining the mixture at a temperature of about 100° C. to 120° C. until the crystals are formed, and separating the crystals from the mother liquor. The crystal material is thereafter washed until the wash effluent has a pH essentially that of wash water and subsequently dried.

ZK-5 is representative of another crystalline aluminosilicate which is prepared in the same manner as zeolite ZK-4 except that N,N'-dimethyltriethylenediammonium hydroxide is used in place of tetramethylammonium hydroxide. ZK-5 may be prepared from an aqueous sodium aluminosilicate mixture having the following composition expressed in terms of oxide mole ratios as:



The N,N'-dimethyltriethylenediammonium hydroxide used in preparing ZK-5 can be prepared by methylating 1,4-diazabicyclo-(2.2.2)-octane with methyl iodide or dimethyl sulfate, followed by conversion to the hydroxide by treatment with silver oxide or barium hydroxide. The reaction may be illustrated as follows:

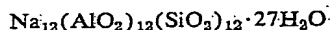


In using the N,N'-dimethyltriethylenediammonium hydroxide compound in the preparation of ZK-5, the hydroxide may be employed per se, or further treated with a source of silica, such as silica gel, and thereafter reacted with aqueous sodium aluminate in a reaction mixture whose chemical composition corresponds to the above-noted oxide mole ratios. Upon heating at temperatures of about 200 to 600° C., the methyl ammonium ion is converted to hydrogen ion.

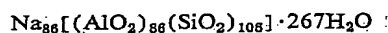
Quite obviously, the above-listed molecular sieves are only representative of the synthetic crystalline aluminosilicate molecular sieve catalysts which may be used in accordance with the process of the present invention, the particular enumeration of such sieves not being intended to be exclusive.

At the present time, two commercially available molecular sieves are those of the "A" series and of the "X" series. A synthetic zeolite known as "Molecular Sieve 4A" is a crystalline sodium aluminosilicate having an ef-

fective pore diameter of about 4 Angstroms. In the hydrated form, this material is chemically characterized by the formula:



The synthetic zeolite known as "Molecular Sieve 5A" is a crystalline aluminosilicate salt having an effective pore diameter of about 5 Angstroms and in which substantially all of the 12 ions of sodium in the immediately above formula are replaced by calcium, it being understood that calcium replaces sodium in the ratio of one calcium ion for two sodium ions. A crystalline sodium aluminosilicate is also available commercially under the name of "Molecular Sieve 13X." The letter "X" is used to distinguish the inter-atomic structure of this zeolite from that of the "A" crystal mentioned above. As initially prepared and before activation by dehydration, the 13X material contains water and has the unit cell formula:



The synthetic zeolite known as "Molecular Sieve 10X" is a crystalline aluminosilicate salt in which a substantial proportion of the sodium ions of the 13X material have been replaced by calcium.

Among the naturally occurring crystalline aluminosilicates which can be employed for purposes of the invention, the preferred aluminosilicates are those which sorb hydrocarbons above C_3 . Exemplary of such aluminosilicates are faujasite, heulandite, clinoptilolite, dachiardite, and aluminosilicates represented as follows:

Chabazite	-----	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 6\text{H}_2\text{O}$
Gmelinite	-----	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 6\text{H}_2\text{O}$
Mordenite	-----	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 6 \cdot 6\text{H}_2\text{O}$

Other aluminosilicates which can be used are those resulting from caustic treatment of various clays.

Of the clay materials, montmorillonite and kaolin families are representative types which include the sub-bentonites, such as bentonite, and the kaolins commonly identified as Dixie, McNamee, Georgia and Florida clays in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays may be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. In order to render the clays suitable for use, however, the clay material is treated with sodium hydroxide or potassium hydroxide, preferably in admixture with a source of silica, such as sand, silica gel or sodium silicate, and calcined at temperatures ranging from 230° F. to 1600° F. Following calcination, the fused material is crushed, dispersed in water and digested in the resulting alkaline solution. During the digestion, materials with varying degrees of crystallinity are crystallized out of solution. The solid material is separated from the alkaline material and thereafter washed and dried. The treatment can be effected by reacting mixtures falling within the following weight ratios:

$\text{Na}_2\text{O}/\text{clay}$ (dry basis)	-----	1.0-6.6 to 1
SiO_2/clay (dry basis)	-----	0.01-3.7 to 1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$ (mole ratio)	-----	35-180 to 1

Molecular sieves are ordinarily prepared initially in the sodium form of the crystal. The sodium ions in such form may, as desired, be exchanged for other cations, as will be described in greater detail below. In general, the process of preparation involves heating, in aqueous solution, an appropriate mixture of oxides, or of materials whose chemical composition can be completely represented as a mixture of oxides Na_2O , Al_2O_3 , SiO_2 and H_2O at a temperature of approximately 100° C. for periods of 15 minutes to 90 hours or more. The product which crystallizes within this hot mixture is separated therefrom and water washed until the water in equilibrium with the zeolite has a pH in the range of 9 to 12. After activating by heating until dehydration is attained, the substance is ready for use.

For example, in the preparation of sodium zeolite "A,"

suitable reagents for the source of silica include silica sol, silica gel, silicic acid or sodium silicate. Alumina can be supplied by utilizing activated alumina, gamma alumina, alpha alumina, aluminum trihydrate or sodium aluminate.

Sodium hydroxide is suitably used as the source of the sodium ion and in addition contributes to the regulation of the pH. All reagents are preferably soluble in water. The reaction solution has a composition, expressed as mixtures of oxides, within the following ranges: $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 0.5 to 2.5; $\text{Na}_2\text{O}/\text{SiO}_2$ of 0.8 to 3.0 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 35 to 200. A convenient and generally employed process of preparation involves preparing an aqueous solution of sodium aluminate and sodium hydroxide and then adding with stirring an aqueous solution of sodium silicate.

The reaction mixture is placed in a suitable vessel which is closed to the atmosphere in order to avoid losses of water and the reagents are then heated for an appropriate length of time. Adequate time must be used to allow for recrystallization of the first amorphous precipitate that forms. While satisfactory crystallization may be obtained at temperatures from 21° C. to 150° C., the pressure being atmospheric or less, corresponding to the equilibrium of the vapor pressure with the mixture at the reaction temperature, crystallization is ordinarily carried out at about 100° C. As soon as the zeolite crystals are completely formed they retain their structure and it is not essential to maintain the temperature of the reaction any longer in order to obtain a maximum yield of crystals.

After formation, the crystalline zeolite is separated from the mother liquor, usually by filtration. The crystalline mass is then washed, preferably with salt-free water, while on the filter, until the wash water, in equilibrium with the zeolite, reaches a pH of 9 to 12. The crystals are then dried at a temperature between 25° C. and 150° C. Activation is attained upon dehydration, as for example at 350° C. and 1 mm. pressure or at 350° C. in a stream of dry air.

It is to be noted that the material first formed on mixing the reactants is an amorphous precipitate which is, generally speaking, not catalytically active in the process of the invention. It is only after transformation of the amorphous precipitate to crystalline form that the highly active catalyst described herein is obtained.

Molecular sieves of the other series may be prepared in a similar manner, the composition of the reaction mixture being varied to obtain the desired ratios of ingredients for the particular sieve in question.

The molecular sieve catalysts useable in the process of the present invention may be in the sodium form as aforesaid or may contain other cations, including other metallic cations and/or hydrogen. In preparing the non-sodium forms of the catalyst composition, the aluminosilicate can be contacted with a non-aqueous or aqueous fluid medium comprising a gas, polar solvent or water solution containing the desired positive ion. Where the aluminosilicate is to contain metal cations, the metal cations may be introduced by means of a salt soluble in the fluid medium. When the aluminosilicate is to contain hydrogen ions, such hydrogen ions may be introduced by means of a hydrogen ion-containing fluid medium or a fluid medium containing ammonium ions capable of conversion to hydrogen ions.

In those cases in which the aluminosilicate is to contain both metal cations and hydrogen ions, the aluminosilicate may be treated with a fluid medium containing both the metal salt and hydrogen ions or ammonium ions capable of conversion to hydrogen ions. Alternatively, the aluminosilicate can be first contacted with a fluid medium containing a hydrogen ion or ammonium ion capable of conversion to a hydrogen ion and then with a fluid medium containing at least one metallic salt. Similarly, the aluminosilicate can be first contacted with a fluid medium containing at least one metallic salt and then with a fluid medium containing a hydrogen ion or an ion capable of conversion to a hydrogen ion or a mixture of both.

Water is the preferred medium for reasons of economy and ease of preparation in large scale operations involving continuous or batchwise treatment. Similarly, for this reason, organic solvents are less preferred but can be employed providing the solvent permits ionization of the acid, ammonium compound and metallic salt. Typical solvents include cyclic and acyclic ethers such as dioxane, tetrahydrofuran, ethyl ether, diethyl ether, diisopropyl ether, and the like; ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate, propyl acetate; alcohols such as ethanol, propanol, butanol, etc.; and miscellaneous solvents such as dimethylformamide, and the like.

The hydrogen ion, metal cation or ammonium ion may be present in the fluid medium in an amount varying within wide limits dependent upon the pH value of the fluid medium. Where the aluminosilicate material has a molar ratio of silica to alumina greater than about 5.0, the fluid medium may contain a hydrogen ion, metal cation, ammonium ion, or a mixture thereof, equivalent to a pH value ranging from less than 1.0 up to a pH value of about 10.0. Within these limits, pH values for fluid media containing a metallic cation and/or an ammonium ion range from 4.0 to 10.0, and are preferably between a pH value of 4.5 to 8.5. For fluid media containing a hydrogen ion alone or with a metallic cation, the pH values range from less than 1.0 up to about 7.0 and are preferably within the range of less than 3.0 up to 6.0. Where the molar ratio of the aluminosilicate is greater than about 3.0 and less than about 5.0, the pH value for the fluid media containing a hydrogen ion or a metal cation ranges from 3.8 to 8.5. Where ammonium ions are employed, either alone or in combination with metallic cations, the pH value ranges from 4.5 to 9.5 and is preferably within the limit of 4.5 to 8.5. When the aluminosilicate material has a molar ratio of silica to alumina less than about 3.0, the preferred medium is a fluid medium containing an ammonium ion instead of a hydrogen ion. Thus, depending upon the silica to alumina ratio, the pH value varies within rather wide limits.

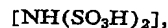
In carrying out the treatment with the fluid medium, the procedure employed comprises contacting the aluminosilicate with the desired fluid medium or media until such time as metallic cations originally present in the aluminosilicate are removed to the desired extent. Repeated use of fresh solutions of the entering ion is of value to secure more complete exchange. Effective treatment with the fluid medium to obtain a modified aluminosilicate having high catalytic activity will vary, of course, with the duration of the treatment and temperature at which it is carried out. Elevated temperatures tend to hasten the speed of treatment whereas the duration thereof varies inversely with the concentration of the ions in the fluid medium. In general, the temperatures employed range from below ambient room temperature of 24° C. up to temperatures below the decomposition temperature of the aluminosilicate. Following the fluid treatment, the treated aluminosilicate is washed with water, preferably distilled water, until the effluent wash water has a pH value of wash water, i.e., between about 5 and 8. The aluminosilicate material is thereafter analyzed for metallic ion content by methods well known in the art. Analysis also involves analyzing the effluent wash for anions obtained in the wash as a result of the treatment, as well as determination of and correction for anions that pass into the effluent wash from soluble substances or decomposition products of insoluble substances which are otherwise present in the aluminosilicate as impurities. The aluminosilicate is then dried and dehydrated.

The actual procedure employed for carrying out the fluid treatment of the aluminosilicate may be accomplished in a batchwise or continuous method under atmospheric, subatmospheric or superatmospheric pressure. A solution of the ions of positive valence in the form of a molten material, vapor, aqueous or non-aqueous solution, may

be passed slowly through a fixed bed of the aluminosilicate. If desired, hydrothermal treatment or a corresponding non-aqueous treatment with polar solvents may be effected by introducing the aluminosilicate and fluid medium into a closed vessel maintained under autogenous pressure. Similarly, treatments involving fusion or vapor phase contact may be employed providing the melting point or vaporization temperature of the acid or ammonium compound is below the decomposition temperature of the aluminosilicate.

A wide variety of acidic compounds can be employed with facility as a source of hydrogen ions and include both inorganic and organic acids.

Representative inorganic acids which can be employed include acids such as hydrochloric acid, hypochlorous acid, chloroplatinic acid, sulfuric acid, sulfurous acid, hydrosulfuric acid, peroxydisulfonic acid ($\text{H}_2\text{S}_2\text{O}_8$), peroxy-monosulfuric acid (H_2SO_5), dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$), sulfamic acid ($\text{H}_2\text{NHS}_3\text{H}$), amidodisulfonic acid



chlorosulfuric acid, thiocyanic acid, hyposulfurous acid ($\text{H}_2\text{S}_2\text{O}_4$), pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$), thiosulfuric acid ($\text{H}_2\text{S}_2\text{O}_3$), nitrosulfonic acid ($\text{HSO}_3\cdot\text{NO}$), hydroxylamine disulfonic acid [$(\text{HSO}_3)_2\text{NOH}$], nitric acid, nitrous acid, hyponitrous acid, carbonic acid and the like.

Typical organic acids which find utility in the practice of the invention include the monocarboxylic, dicarboxylic and polycarboxylic acids which can be aliphatic, aromatic or cycloaliphatic in nature.

Representative aliphatic monocarboxylic, dicarboxylic and polycarboxylic acids include the saturated and unsaturated, substituted and unsubstituted acids such as formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, propionic acid, 2-bromopropionic acid, 3-bromopropionic acid, lactic acid, ni-butyric acid, isobutyric acid, crotonic acid, n-valeric acid, isovaleric acid, n-caproic acid, oenanthic acid, pelargonic acid, capric acid, undecyclic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, alkylsuccinic acid, alkenylsuccinic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, glutonic acid, muconic acid, ethylidene malonic acid, isopropylidene malonic acid, allyl malonic acid.

Representative aromatic and cycloaliphatic monocarboxylic, dicarboxylic and polycarboxylic acids include 1,2-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 2-carboxy-2-methylcyclohexanecarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,8-naphthalenedicarboxylic acid, 1,2-naphthalenedicarboxylic acid, tetrahydrophthalic acid, 3-carboxy-cinnamic acid, hydrocinnamic acid, pyrogalllic acid, benzoic acid, ortho, meta and para-methyl, hydroxy, chloro, bromo and nitro-substituted benzoic acids, phenylacetic acid, mandelic acid, benzylic acid, hippuric acid, benzenesulfonic acid, toluenesulfonic acid, methanesulfonic acid and the like.

Other sources of hydrogen ions include carboxy polyesters prepared by the reaction of an excess of polycarboxylic acid or an anhydride thereof and a polyhydric alcohol to provide pendant carboxyl groups.

Still other materials capable of providing hydrogen ions are ion exchange resins having exchangeable hydrogen ions attached to base resins comprising cross-linked resinous polymers of monovinyl aromatic monomers and polyvinyl compounds. These resins are well known materials which are generally prepared by copolymerizing in the presence of a polymerization catalyst one or more monovinyl aromatic compounds, such as styrene, vinyl toluene, vinyl xylene, with one or more divinyl aromatic compounds such as divinyl benzene, divinyl toluene, divinyl xylene, divinyl naphthalene and divinyl acetylene. Following copolymerization, the resins are sulfonated to provide the hydrogen form of the resin.

Still another class of compounds which can be employed are ammonium compounds which decompose to provide hydrogen ions when an aluminosilicate treated with a solution of said ammonium compound is subjected to temperatures below the decomposition temperature of the aluminosilicate.

Representative ammonium compounds which can be employed include ammonium hydroxide; ammonium chloride; ammonium bromide; ammonium iodide; ammonium carbonate; ammonium bicarbonate; ammonium sulfate; ammonium sulfide; ammonium thiocyanate; ammonium dithiocarbamate; ammonium peroxysulfate; ammonium acetate; ammonium tungstate; ammonium molybdate; ammonium benzoate; ammonium borate; ammonium carbamate; ammonium sesquicarbonate; ammonium chloroplumbate; ammonium citrate; ammonium dithionate; ammonium fluoride; ammonium gallate; ammonium nitrate; ammonium nitrite; ammonium formate; ammonium propionate; ammonium butyrate; ammonium valerate; ammonium lactate; ammonium malonate; ammonium oxalate; ammonium palmitate; ammonium tartrate and the like. Still other ammonium compounds which can be employed include complex ammonium compounds such as tetraethylammonium hydroxide; trimethylammonium chloride. Other compounds which can be employed are nitrogen bases such as the salts of guanidine, pyridine, quinoline, etc.

A wide variety of metallic compounds can be employed with facility as a source of metallic cations and include both inorganic and organic salts of the metals of Groups I through VIII of the Periodic Table.

Representative of the salts which can be employed include chlorides, bromides, iodides, carbonates, bicarbonates, sulfates, sulfides, thiocyanates, dithiocarbamates, peroxysulfates, acetates, benzoates, citrates, fluorides, nitrates, nitrites, formates, propionates, butyrate, valerates, lactates, malonates, oxalates, palmitates, hydroxides, tartrates, and the like. The only limitation on the particular metal salt or salts employed is that it be soluble in the fluid medium in which it is used. The preferred salts are the chlorides, nitrates, acetates and sulfates.

Rare earth salts may be advantageously employed. Such salts can either be the salt of a single metal, or, preferably, of mixtures of metals such as a rare earth chloride or didymium chlorides. As hereinafter referred to, a rare earth chloride solution is a mixture of rare earth chlorides consisting essentially of the chlorides of lanthanum, cerium, neodymium and praseodymium with minor amounts of samarium, gadolinium and yttrium. The rare earth chloride solution is commercially available and it contains the chlorides of a rare earth mixture having the relative composition: cerium (as CeO_2) 48% by weight; lanthanum (as La_2O_3) 24% by weight; praseodymium (as Pr_6O_{11}) 5% by weight; neodymium (as Nd_2O_3) 17% by weight; samarium (as Sm_2O_3) 3% by weight; gadolinium (as Gd_2O_3) 2% by weight; yttrium (as Y_2O_3) 0.2% by weight; and other rare earth oxides 0.8% by weight didymium chloride is also a mixture of rare earth chlorides, but having a low cerium content. It consists of the following rare earths determined as oxides: lanthanum, 45-46% by weight; cerium, 1-2% by weight; praseodymium, 9.10% by weight; neodymium, 32-33% by weight; samarium, 5-6% by weight; gadolinium, 3-4% by weight; yttrium, 0.4% by weight; other rare earths, 1-2% by weight. It is to be understood that other mixtures of rare earths are equally applicable in the instant invention.

Representative metal salts which can be employed, aside from the mixture mentioned above, include silver nitrate, silver acetate, silver arsenate, silver citrate, silver oxide, silver tartrate, calcium acetate, calcium arsenate, calcium benzoate, calcium bromide, calcium carbonate, calcium chloride, calcium citrate, beryllium bromide, beryllium carbonate, beryllium hydroxide, beryllium sulfate, barium acetate, barium bromide, barium carbonate,

barium citrate, barium malonate, barium nitrite, barium oxide, barium sulfide, magnesium chloride, magnesium bromide, magnesium sulfate, magnesium sulfide, magnesium acetate, magnesium formate, magnesium stearate, magnesium tartrate, manganese chloride, manganese sulfate, manganese acetate, manganese carbonate, manganese formate, zinc nitrate, zinc acetate, zinc chloride, zinc bromide, aluminum chloride, aluminum bromide, aluminum acetate, aluminum citrate, aluminum nitrate, aluminum oxide, aluminum phosphate, aluminum sulfate, titanium bromide, titanium chloride, titanium nitrate, titanium sulfate, zirconium chloride, zirconium nitrate, zirconium sulfate, chromic acetate, chromic chloride, chromic nitrate, chromic sulfate, ferric chloride, ferric bromide, ferric acetate, ferrous chloride, ferrous arsenate, ferrous lactate, ferrous sulfate, nickel chloride, nickel bromide, cerous acetate, cerous bromide, cerous carbonate, cerous chloride, cerous iodide, cerous sulfate, cerous sulfide, lanthanum chloride, lanthanum bromide, lanthanum nitrate, lanthanum sulfate, lanthanum sulfide, yttrium bromate, yttrium bromide, yttrium chloride, yttrium nitrate, yttrium sulfate, samarium acetate, samarium chloride, samarium bromide, samarium sulfate, neodymium chloride, neodymium oxide, neodymium sulfide, neodymium sulfate, praseodymium chloride, praseodymium bromide, praseodymium sulfate, praseodymium sulfide, selenium chloride, selenium bromide, tellurium chloride, tellurium bromide, etc.

The aluminosilicate catalysts useable in connection with the process of the present invention may be used in powdered, granular or molded state formed into spheres or pellets of finely divided particles having a particle size of 2 to 500 mesh. In cases where the catalyst is molded, such as by extrusion, the aluminosilicate may be extruded before drying, or dried or partially dried and then extruded. The catalyst product is then preferably precalcined in an inert atmosphere near the temperature contemplated for conversion but may be calcined initially during use in the conversion process. Generally, the aluminosilicate is dried between 150° F. and 600° F. and thereafter calcined in air or an inert atmosphere of nitrogen, hydrogen, helium, flue gas or other inert gas at temperatures ranging from about 500° F. to 1500° F. for periods of time ranging from 1 to 48 hours or more.

The aluminosilicate catalysts prepared in the foregoing manner may be used as catalysts per se or as intermediates in the preparation of further modified contact masses consisting of inert and/or catalytically active materials which otherwise serve as a base, support, carrier, binder, matrix or promoter for the aluminosilicate. One embodiment of the invention is the use of the finely divided aluminosilicate catalyst particles in a siliceous gel matrix wherein the catalyst is present in such proportions that the resulting product contains about 2 to 95% by weight, preferably about 5 to 50% by weight, of the aluminosilicate in the final composite.

The aluminosilicate-siliceous gel compositions can be prepared by several methods wherein the aluminosilicate is combined with silica while the latter is in a hydrous state such as in the form of a hydrosol, hydrogel, wet, gelatinous precipitate or a mixture thereof. Thus, silica gel formed by hydrolyzing a basic solution of alkali metal silicate with an acid such as hydrochloric, sulfuric, etc., can be mixed directly with finely divided aluminosilicate having a particle size less than 40 microns, preferably within the range of 2 to 7 microns. The mixing of the two components can be accomplished in any desired manner, such as in a ball mill or other types of kneading mills. Similarly, the aluminosilicate may be dispersed in a hydrosol obtained by reacting an alkali metal silicate with an acid or an alkaline coagulant. The hydrosol is then permitted to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired shape, or dispersed through a nozzle into a bath of oil or other water-immiscible suspending medium to obtain spheroidally

shaped "bead" particles of catalyst. The aluminosilicate siliceous gel thus obtained is washed free of soluble salts and thereafter dried and/or calcined as desired.

The siliceous gel matrix may also consist of a plural gel comprising a predominant amount of silica with one or more metals or oxides thereof. The preparation of plural gels is well known and generally involves either separate precipitation or coprecipitation techniques in which a suitable salt of the metal oxide is added to an alkali metal silicate and an acid or base, as required, is added to precipitate the corresponding oxides. The silica content of the siliceous gel matrix contemplated herein is generally with the range of 55 to 100 weight percent with the metal oxide content ranging from zero to 45 percent. Minor amounts of promoters or other materials which may be present in the composition include cerium, chromium, cobalt, tungsten, uranium, platinum, lead, zinc, calcium, magnesium, lithium, silver, nickel and their compounds.

The aluminosilicate catalyst may also be incorporated in an alumina gel matrix conveniently prepared by adding ammonium hydroxide, ammonium carbonate, etc. to a salt of aluminum, such as aluminum chloride, aluminum sulfate, aluminum nitrate, etc., in an amount to form aluminum hydroxide, which, upon drying, is converted to alumina. The aluminosilicate catalyst can be mixed with the dried alumina or combined while the alumina is in the form of a hydrosol, hydrogel or wet gelatinous precipitate.

While, as aforesaid, the ester exchange reactions of the present invention may be carried out using a great variety of solid porous crystalline aluminosilicate zeolites as catalytic materials, most effective results are obtained through the use of acidic zeolites such as the rare earth exchanged 13X, the hydrogen Y and the calcium exchanged 10X molecular sieves. Also extremely effective are the high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio Y type molecular sieves (i.e., above about 5:1), particularly those of the acid, rare earth exchanged or calcium exchanged variety.

For maximum effectiveness in carrying out the ester exchange, reactions of the present invention, the crystalline aluminosilicate used as a catalyst should have pores or channels of a size such that the reactants will pass into such pores or channels and the reaction product will be

tions within the present invention may be carried out at temperatures from about 50 to 300° C. and at atmospheric or elevated pressures.

The following examples are illustrative of the general process of the present invention:

Example 1

In a three-necked one-liter flask there is placed 400 ml. of vinyl acetate, 200 grams of stearic acid and 20 grams of rare earth exchanged hydrogen 13X molecular sieve. The flask is fitted with an efficient condenser, thermometer and stirring device. The stirred mixture is then heated at reflux for six hours. The hot solution is filtered to remove catalyst and then stripped of volatiles (acetic acid and vinyl acetate) by distillation at 100° C. under 1 mm. vacuum. The residual crude vinyl stearate weighs 220 grams and has an iodine number of 80.

Example 2

Three hundred parts of methyl oleate and 30 parts of a hydrogen Y crystalline aluminosilicate



are placed in a 1-liter four-necked flask fitted with a mercury-sealed stirrer, thermometer, dropping funnel and a Vigreux column leading to a take-off condenser. The mixture is heated to 90° C. and 75 parts of triacetin is added in 30 minutes. Methyl acetate distills out of the reactants through the Vigreux column. After 3 hours about 72 parts of methyl acetate is collected indicating nearly complete reaction. The saponification number of the residue is 200.

Examples 3-5

In the experiments recorded in Table I, 50 grams of dimethylterephthalate and 50 grams of ethylene glycol are placed in a flask together with the amount of catalyst indicated in the table. The flask is fitted with a Vigreux column take-off to a receiver to collect methanol formed during the reaction. Evolution of methanol begins at 150° C. Heating is continued 1-2 hours during which time methanol is evolved and collected and the pot temperature rises from 150 to 220° C. The temperature is then raised to 270° C. and vacuum (1 mm.) is applied. The polymer formed thusly is analyzed for degree of polymerization using a capillary viscometer.

TABLE I

Experiment	Catalyst, Wt. Percent	Hours, Polymerization Time	Relative Viscosity ¹
3	Rare Earth Hydrogen X, 5%	3	28
4	do	5	38
5	Rare Earth Hydrogen X, 10%	3	33

¹ Viscosity of a solution of 11 g. of polymer in 100 cc. of mixed solvent consisting of 7 parts of trichlorophenol and ten parts of phenol and then relating the viscosity of this polymer solution to the viscosity of the mixed solvent according to the formula:

$$\text{Relative viscosity} = \frac{\text{efflux time for the solution}}{\text{efflux time for the solvent}}$$

Example 6

A mixture of 136 parts of phenylacetate, 136 parts of methyl benzoate and 25 parts of rare earth exchanged 13X molecular sieve are placed in a one liter, three-necked flask fitted with a stirrer, thermometer and a Vigreux column attached to a take-off condenser for removing volatile constituents. The mixture is heated to 100° C. and held at that temperature until all of the methyl acetate formed by the reaction has been removed. This normally requires about five hours. The residue is substantially pure phenylbenzoate and can be recrystallized from cyclohexane to give high purity product, M.P. 70-71° C.

Example 7

Methyl sebacate, 230 parts, 2-ethylhexanol, 260 parts, and hydrogen Y molecular sieve, 85 parts, are stirred and heated at 140° C. in a flask fitted with a device for

removable therefrom. Quite obviously, the particular pore size which is desirable will vary depending upon the particular starting materials utilized and the products to be formed as a result of the reaction. In general, however, it can be stated that the most desirable crystalline aluminosilicates for use in the instant process are those having a pore size of at least about 5 Angstrom units, though such pore size could be smaller if the starting materials and reaction products are not too highly substituted. Highly desirable results are obtained with pore sizes of about 5-15 A. with pore sizes of about 6-13 A. being particularly preferred.

The reaction conditions under which the esterification reactions of the present invention may be carried out will necessarily vary depending upon whether the reaction is of the trans-esterification, alcoholysis or acidolysis variety and, even within such categories, the nature of the starting materials. Generally speaking, the esterification reac-

removing methanol as it is formed during the reaction. After six hours at 140° C. there is collected 70 ml. of methanol. The product, di-2-ethylhexyl sebacate, weighed 10 grams and could be distilled under vacuum to obtain high purity ester.

Examples 8-12

The following table (Table II) describes several experiments wherein ethylene diacetate is reacted with alcohols in the presence of crystalline aluminosilicate catalysts:

TABLE II

Example No.	Moles, Ethylene Diacetate	Alcohol		Crystalline aluminosilicate catalyst		Temp., °C.	Time, Hrs.	Products, moles	
		Kind	Moles	Kind	Wt. Percent			Alkyl Acetate	Glycol Mono-Acetate
1	1	Ethyl	2	None		88	18	Trace	Trace
1	1	do.	1	REHX		80	5	0.8	0.9
0	1	Isopropyl	1	REHX	5	90	5	0.3	0.5
1	1	Ethyl	1	EY	5	90	5	0.8	0.9
2	1	n-butyl	1	EY	6	100	5	0.8	0.8

* REHX is the abbreviation for the rare earth exchanged hydrogen 13X molecular sieve which was used in Example 1.

* EY is the abbreviation for the hydrogen Y crystalline aluminosilicate used in Example 2.

In the foregoing portion of the specification, a novel process for conducting an ester exchange reaction by means of crystalline aluminosilicate catalysts has been set forth. It is to be understood, however, that the practice of the present invention is also applicable to isomorphs of said crystalline aluminosilicates. For example, the aluminum may be replaced by elements such as gallium and silicon by elements such as germanium.

It is to be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

What is claimed is:

1. In a process of conducting an ester interchange reaction between an ester of a carboxylic acid and a compound selected from the group consisting of carboxylic acids, alcohols and esters of carboxylic acids, the improvement which comprises carrying out said ester interchange in the presence of a solid porous crystalline aluminosilicate zeolite catalyst.

2. A process as defined in claim 1 wherein said alu-

minosilicate catalyst contains pores of at least about 5 Å.

3. A process as defined in claim 2 wherein said aluminosilicate catalyst contains pores of about 6 to 13 Å.

4. A process as defined in claim 1 wherein said aluminosilicate is acidic.

5. A process as defined in claim 4 wherein said aluminosilicate is rare earth exchanged.

6. A process as defined in claim 1 wherein said aluminosilicate is rare earth exchanged.

7. A process as defined in claim 1 wherein said aluminosilicate is calcium exchanged.

8. A process as defined in claim 1 wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of said aluminosilicate is at least about 5:1 and said aluminosilicate is faujasitic in its crystal structure.

9. In a process of conducting an ester interchange reaction between an ester of a carboxylic acid and a compound selected from the group consisting of carboxylic acids, alcohols and esters of carboxylic acids, the improvement which comprises carrying out said ester interchange in the presence of a catalyst selected from the group consisting of solid porous crystalline aluminosilicate zeolites and isomorphs thereof.

References Cited

UNITED STATES PATENTS

2,521,742 9/1950 Paterson 260-410.9
3,023,183 2/1962 Nelson 260-410.9

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